

CLAIMS

1. A cosmetic composition containing, in a physiologically acceptable medium, at least one rod-coil type block copolymer comprising at least one "coil" 5 polymeric block structure of variable conformation bonded to at least one "rod" block structure of restricted conformation, the composition being characterized in that said rod block structure is of polymeric nature and is constituted in full or in part of peptide motifs or the 10 like with some or all of the free hydrogen atoms of said peptide motifs participating in non-covalent hydrogen bonds within the rod structure.

2. A composition according to claim 1, characterized in 15 that the non-covalent hydrogen bonds within the rod structure are present in sufficient number and/or are strategically placed as to ensure that said rod polymeric structure has a mean distance between the ends of its chain $\langle R_0^2 \rangle$ satisfying the convention:

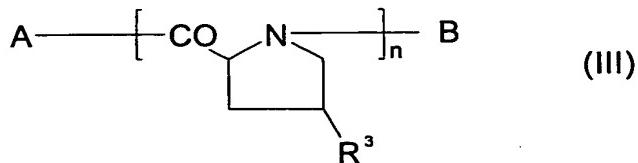
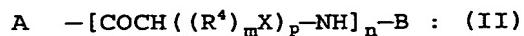
$$20 \quad \langle R_0^2 \rangle_{\text{rod}} = CN L^2$$

where:

L represents the length of a monomer;
C represents the restrictions imposed on the chain with C greater than 1 and in particular lying in the 25 range 4 to 10; and

N represents the number of monomers constituting the block.

3. A composition according to claim 1 or claim 2, 30 characterized in that the rod polymeric block structure satisfies in full or in part general formula (II) or (III):



in which:

- n represents an integer not less than 3;
- m represents an integer lying in the range 0 to 30;
- 5 • p represents an integer lying in the range 0 to 1:
- X represents:
 - OR¹;
 - N R¹ R²;
 - COOR¹;
 - 10 • NH-C(NH)NR¹R²;
 - an optionally condensed heterocycle possibly including 1 to 2 nitrogen atoms and being unsaturated;
 - S R¹;
 - OCOR¹;
 - 15 • OCONR¹R²;
 - OCOOR¹;
 - CONR¹R²;
 - NR¹COR²;
 - NR¹COO R²;
 - 20 • PO(OR¹)₂;
 - SS R¹;
 - SCOR¹;
 - SCOO R¹; or
 - SO₃H;
 - 25 • R¹, R², and R³ represent independently of one another:
 - a hydrogen atom;
 - a linear alkyl grouping, in particular in the range C₁ to C₁₂, more particularly C₂ to C₈, branched, 30 where appropriate cyclic; or
 - an aromatic grouping, in particular aryl, aralkyl, alkylaryl, or diaryl, in the range C₁ to C₃₀, e.g. of the benzyl type;
 - R⁴ represents a divalent linear alkylene grouping in particular in the range C₁ to C₁₂, more particularly C₂ to C₈, that is branched, possibly cyclic, or an aromatic grouping, in particular arylene, aralkylene, or

alkylarylene, or diarylene in the range C₁ to C₃₀, e.g. of the benzylene type

with R⁴, m, and X possibly having respective different meanings within the general formula (II);

5 · A represents a hydroxyl or derived function, represents the bond established with a coil block structure, or represents a function capable of initiating peptide polymerization;

10 · B represents a hydrogen atom or represents the bond established with a coil block structure; and

- derivatives thereof.

4. A composition according to claim 3, characterized in that said rod-coil block polymer satisfies formula (II) in which:

15 · m represents an integer in the range 0 to 12;

- X represents a grouping selected from -O R¹, -NR¹R², -COOR¹, -NR¹COR², -CONR¹R², -NR¹COO R², or -SR¹; with R¹ and R² representing independently of each other a

20 hydrogen atom, a methyl, ethyl, propyl, butyl, isobutyl, isopropyl, phenyl, benzyl, trifluoromethyl, -(CH₂)₂OH or -(CH₂)₃OH group.

25 5. A composition according to any one of claims 1 to 4, characterized in that the rod block structure is derived from homopolymerization or copolymerization of one or more amino acids selected from the group consisting in glycine, alanine, phenylalanine, valine, isoleucine, leucine, arginine, asparagine, aspartic acid, cysteine,

30 methionine, glutamine, glutamic acid, histidine, lysine, serine, threonine, tryptophane, tyrosine, proline, and derivatives thereof.

35 6. A composition according to any one of claims 1 to 5, characterized in that the rod-block structure is or is derived from:

- poly(L-leucine), poly(L-valine),
poly(phenylalanine);
 - poly(L-lysine) and derivatives thereof, such as
poly(N-benzyloxycarbonyl-L-lysine) and poly(N-
5 trifluoroacetyl-L-lysine), and derivatives thereof such
as hydrochlorides;
 - poly(L-glutamic acid) and salts thereof such as
the sodium salt, and derivatives thereof, such as poly γ -
alkylesters in the range C₁-C₃₀ of L-glutamic acid such as
10 poly(γ -methyl-L-glutamate) or poly γ -aryl esters in the
range C₁-C₃₀ or poly γ -alkyl aryl esters in the range C₁-C₃₀
such as poly(γ -benzyl-L-glutamate);
 - polyglutamine and derivatives thereof, such as
poly(N-hydroxyethyl-L-glutamine and poly(N-hydroxypropyl-
15 L-glutamine); and
 - polypeptide copolymers of the above monomers of
the poly(hydroxyethyl-L-glutamine and leucine),
poly(hydroxyethyl-L-glutamine and valine), poly(γ -benzyl-
L-glutamate and leucine), poly(γ -benzyl-L-glutamate and
20 D,L-phenylalanine, poly(γ -benzyl-L-glutamate and
cinnamylglutamate), poly(N-benzyloxycarbonyl-L-lysine and
 γ -benzyl-L-glutamate) type, and salts and derivatives
thereof.
- 25 7. A composition according to any one of claims 1 to 6,
characterized in that the number average molecular mass
of the rod blocks lies in the range 200 g/mol to
1,000,000 g/mol, in particular 250 g/mol to
800,000 g/mol, and more particularly 250 g/mol to
30 500,000 g/mol.
- 35 8. A composition according to any one of claims 1 to 7,
characterized in that the rod blocks are present at at
least 10%, in particular at least 15%, or at least 30%,
and in particular at most 90%, or at most 85%, or at most

80% by weight relative to the total weight of the copolymer.

9. A composition according to any one of claims 1 to 8,
5 characterized in that the mean distance between the ends
of a chain in the coil block, i.e. $\langle R_0^2 \rangle_{coil}$ satisfies the
convention:

$$\langle R_0^2 \rangle_{coil} = N L^2$$

where N and L are as defined in claim 2.

- 10 10. A composition according to any one of claims 1 to 9,
characterized in that the coil block is made of one or
more copolymers or homopolymers derived from radical
polymerization of monomers comprising ethylene, vinyl,
15 allyl, (meth)acrylate, and/or (meth)acrylamide motifs and
derivatives thereof.

11. A composition according to any one of claims 1 to 10,
characterized in that the coil polymer is selected from:

- 20 • vinyl and (meth)acrylate, vinyl and
(meth)acrylamide, vinyl and (meth)acrylate and
(meth)acrylamide, olefin and vinyl, and (meth)acrylate
and (meth)acrylamide copolymers, and also (meth)acrylate
and (meth)acrylate copolymers.
- 25 • homopolymers or copolymers based on vinyl acetate,
styrene, vinylpyrrolidone, vinylcaprolactam, ethylene
polyoxide (meth)acrylate, stearyl (meth)acrylate, lauryl
(meth)acrylate, vinyl laurate, butyl (meth)acrylate,
ethylhexyl (meth)acrylate, crotonic acid, (meth)acrylic
30 acid, maleic anhydride, sulfonic styrene acid,
dimethyldiallylamine, vinylpyridine, dimethylaminoethyl
(meth)acrylate, dimethylaminopropyl (meth)acrylamide, and
salts thereof;
- 35 • polycondensates of polyurethane and/or polyureas,
aliphatic polyesters, aliphatic polyamides, and
copolymers thereof;

· polycondensates of polyurethane and/or polyureas, of aliphatic polyesters, of aliphatic polyamides or of their copolymers, such as for example polycondensates of poly(urethane/urea) and poly(ester/amide);

5 · polymers obtained by cycle opening, selected from polyethers of the ethylene polyoxide type, propylene polyoxide and copolymers thereof, polylactides, polyesters such as polycaprolactone; and polyoxazolines such as poly(2-methyloxazoline), or poly(2-
10 ethyloxazoline);

· homopolymers of siloxane, such as polydimethylsiloxane (PDMS), polymethylphenylsiloxane, and polymethyllaurylsiloxane;

15 · polymers obtained by metathesis such as poly(norbornene) and copolymers thereof;

· polymers obtained by cationic polymerization such as polyvinylalkylethers e.g. polyvinylmethylethers;

· copolymers of different types of the above polymers;

20 · copolymers of different types of the above polymers with other polymers, such as for example polysiloxanes and ethylene polyoxide copolymers; and

· salts and derivatives thereof.

25 12. A composition according to any one of claims 1 to 11, characterized in that the number average molecular mass of the coil block lies in the range 300 g/mol to 1,000,000 g/mol, in particular 500 g/mol to 800,000 g/mol, and more particularly 500 g/mol to
30 500,000 g/mol.

13. A composition according to any one of claims 1 to 12, characterized in that its overall number average molecular mass lies in the range 700 g/mol to 1,000,000 g/mol, in particular 1,000 g/mol to 800,000 g/mol, and more particularly 2,000 g/mol to 500,000 g/mol.

14. A composition according to any one of claims 1 to 13, characterized in that said rod-coil block copolymer is not cross-linked.

5

15. A composition according to any one of claims 1 to 14, characterized in that said rod-coil copolymer is selected from the group comprising:

- rod-block-coil (also abbreviated as rod -b- coil)
- 10 di-block, such as for example ethylene polyoxide -b- poly(gamma benzyl L-glutamate), poly(N-benzyloxycarbonyl-L-lysine) -b- ethylene polyoxide, ethylene polyoxide -b- poly(gamma L-glutamic acid), polyL-lactide -b- poly(gamma benzyl L-glutamate), ethylene polyoxide -b- poly(gamma benzyl L-glutamate), poly(gamma benzyl lysine) -b- polystyrene, polydimethylsiloxane -b- poly(L glutamic acid), acrylic polyacid -b- poly(L-glutamic acid), sulfonic polyester -b- poly(L-glutamic acid), poly(gamma methyl-L glutamate) -b- polyurethane, polyethylene imine
- 15 -b- poly(L-phenylalanine), polymethyloxazoline -b- poly(L-phenylalanine), polycaprolactone -b- poly(L-alanine), polycaprolactone -b- polyglycine, polybutadiene -b- poly(L-glutamic acid), polydimethylsiloxane -b- poly(benzyl-glutamate), poly(N-benzyloxycarbonyl-L-lysine) -b- poly(ethylene oxide co propylene oxide),
- 20 poly(ethylene oxide co propylene oxide) -b- poly gamma L-glutamic acid, poly(ethylene oxide co propylene oxide) -b- poly(gamma benzyl L-glutamate), and salts thereof;
- 25 • coil-block-rod-block-coil or rod -b- coil -b- rod
- 30 tri-blocks such as for example poly(gamma benzyl L-glutamate) -b- polystyrene -b- poly(gamma benzyl L-glutamate), poly(L-glutamic acid) -b- polybutadiene -b- poly(L-glutamic acid), poly(L-glutamic acid) -b- polydimethylsiloxane -b- poly(L-glutamic acid),
- 35 poly(gamma benzyl L-glutamate) -b- poly(ethylene oxide or co propylene oxide) -b- poly(gamma benzyl L-glutamate), poly(benzyl-glutamate) -b- polydimethylsiloxane -b-

- poly(benzyl-glutamate), poly(L-glutamic acid) -b- acrylic polyacid -b- poly(L-glutamic acid), poly(L-glutamic acid) -b- sulfonic polyester -b- poly(L-glutamic acid),
5 poly(gamma methyl-L glutamate) -b- polyurethane -b- poly(gamma methyl-L glutamate; poly(L-phenylalanine) -b- imine polyethylene -b- poly(L-phenylalanine), poly(L-phenylalanine) -b- polymethyloxazoline -b- poly(L-phenylalanine), poly(L-alanine) -b- polycaprolactone -b- poly(L-alanine), polyglycine -b- polycaprolactone -b-
10 polyglycine, poly(L-valine) -b- poly(ethylene oxide co propylene oxide) -b- poly(L-valine), and salts thereof.
16. A composition according to any preceding claim, characterized in that it contains 0.5% by weight to 90%
15 by weight, in particular 0.7% by weight to 85% by weight, and more particularly 0.8% by weight to 75% by weight of copolymer(s) relative to the total weight of the composition.
- 20 17. A composition according to any preceding claim, characterized in that it includes at least one aqueous phase.
18. A composition according to any preceding claim,
25 characterized in that said composition includes at least one fatty phase.
19. A composition according to any one of claims 1 to 16 and 18, characterized in that it is anhydrous.
30
20. A composition according to claim 18 or claim 19, characterized in that said fatty phase contains at least one fat that is liquid at ambient temperature and at atmospheric pressure, and/or at least one fat that is solid at ambient temperature and at atmospheric pressure.
35

21. A composition according to claim 20, characterized in that said fat that is liquid at ambient temperature and at atmospheric pressure comprises at least one volatile or non-volatile oil or a mixture thereof.

5

22. A composition according to claim 20 or claim 21, characterized in that said fat that is liquid at ambient temperature and at atmospheric pressure represents 0.01% to 90% by weight, and in particular 0.1% to 85% by weight relative to the total weight of the fatty phase.

10

23. A composition according to any one of claims 20 to 22, characterized in that said fat that is solid at ambient temperature and at atmospheric pressure is selected from waxes, pasty fats, gums, and mixtures thereof.

15

24. A composition according to any one of claims 18 to 23, characterized in that said fatty phase contains at least one solid fat constituting 0.01% to 50%, in particular 0.1% to 40%, and more particularly 0.2% to 30% by weight relative to the total weight of the composition.

25

25. A composition according to any preceding claim, characterized in that said composition further comprises a particulate phase constituting 0.01% to 40%, in particular 0.01% to 30%, and more particularly 0.05% to 20% by weight relative to the total weight of said composition.

30

26. A composition according to claim 25, characterized in that said particulate phase comprises at least one additional pigment and/or nacre and/or filler.

35

27. A composition according to any one of claims 1 to 18 and 20 to 26, characterized in that it is in the form of an oil-in-water or a water-in-oil emulsion.
- 5 28. A composition according to any preceding claim, characterized in that it is in the form of a product that has been cast as a stick or a cake.
- 10 29. A composition according to any preceding claim, characterized in that it is in the form of a makeup and/or a care product for the skin and/or the lips.
- 15 30. A composition according to any one of claims 1 to 27, characterized in that it is in the form of a care product and/or a makeup for the nails.
31. A composition according to any one of claims 1 to 27, characterized in that it is in the form of a care product and/or a styling composition for the hair.
- 20 32. A method of cosmetically treating a keratinous material comprising at least applying a composition according to any one of claims 1 to 31 on said material.
- 25 33. The use of a copolymer as defined in any one of claims 1 to 15 as a surface active agent.
34. The use of a copolymer as defined in any one of claims 1 to 15 as a rheological agent.
- 30 35. A block copolymer of the rod-coil type comprising at least one "coil" polymeric block structure of variable conformation bonded to at least one "rod" block structure of restricted conformation, the copolymer being characterized in that said rod block structure is of polymeric nature and is constituted in full or in part by peptide motif(s) or the like with all or some of the free

hydrogen atoms of said peptide motifs participating in non-covalent hydrogen bonds within the rod structure, and in that said coil block is made up of:

- radical homo- or copolymers derived from radical polymerization of at least one ethylene monomer of at least one of the following types: butadiene, (meth)acrylic, (meth)acrylamide, allyl, vinyl alcohol ester, and vinyl ether;
- polycondensates of polyurethane and/or polyureas, of aliphatic polyesters, of aliphatic polyamides, or copolymers thereof, such as, for example, polycondensates of poly(urethane/urea) and poly(ester/amide);
- polymers obtained by opening cycles selected from polyesters such as polycaprolactone, and polyoxazolines such as poly(2-methyloxazoline), or poly(2-ethyloxazoline);
- homopolymers of siloxane, such as for example polydimethylsiloxane (PDMS), and polymethylphenylsiloxane or polymethyllaurylsiloxane;
- polymers obtained by metathesis such as poly(norbornene) and copolymers thereof;
- copolymers comprising monomers obtained by cationic polymerization such as polyvinylalkylethers such as for example polyvinylmethylethers;
- copolymers of different types of the above polymers such as, for example poly(urethane siloxane);
- copolymers of different types of the above polymers with other copolymers such as, for example copolymers of polysiloxane and ethylene polyoxide; and
- salts and derivatives thereof.

36. A copolymer according to claim 35, characterized in that the rod block is as defined in claims 2 to 8.

35 37. A copolymer according to claim 35 or claim 36, characterized in that the coil block is as defined in claims 12 to 14.

38. A copolymer, characterized in that it is selected from the group comprising:

- rod-block-coil di-blocks such as poly(N-
- 5 benzyloxycarbonyl L-lysine) -b- ethylene polyoxide, ethylene polyoxide -b- poly gamma L-glutamic acid, poly L-lactide -b- poly(gamma benzyl L-glutamate), ethylene polyoxide -b- poly(gamma benzyl L-glutamate), poly(gamma benzyl lysine) -b- polystyrene, polydimethylsiloxane -b-
- 10 poly(L-glutamic acid), acrylic polyacid -b- poly(L-glutamic acid), sulfonic polyester -b- poly(L-glutamic acid), poly(gamma methyl L-glutamate) -b- polyurethane polyethylene imine -b- poly(L-phenylalanine), polymethyloxazoline -b- poly(L-phenylalanine),
- 15 polycaprolactone -b- poly(L-alanine), polycaprolactone -b- polyglycine, polybutadiene -b- poly(L-glutamic acid) polydimethylsiloxane -b- poly(benzyl-glutamate), poly(N-benzyloxycarbonyl L-lysine) -b- poly(ethylene oxide co propylene oxide), poly(ethylene oxide co propylene oxide)
- 20 -b- poly gamma L-glutamic acid, poly(ethylene oxide co propylene oxide) -b- poly(gamma benzyl L-glutamate), and salts thereof;
- coil-block-rod-block-coil tri-blocks or rod -b- coil -b- rod tri-blocks such as poly(gamma benzyl L-
- 25 glutamate) -b- propylene polyoxide -b- poly(gamma benzyl L-glutamate), poly(gamma benzyl L-glutamate) -b- polystyrene -b- poly(gamma benzyl L-glutamate), poly(L-glutamic acid) -b- polybutadiene -b- poly(L-glutamic acid), poly(L-glutamic acid) -b- polydimethylsiloxane -b-
- 30 poly(L-glutamic acid), poly(L-glutamic acid) -b- polydimethylsiloxane -b- poly(L-glutamic acid) poly(gamma benzyl L-glutamate) -b- poly(ethylene oxide co propylene oxide) -b- poly(gamma benzyl L-glutamate), poly(benzyl-glutamate) -b- polydimethylsiloxane -b- poly(benzyl-
- 35 glutamate), poly(L-glutamic acid) -b- acrylic polyacid -b- poly(L-glutamic acid), poly(L-glutamic acid) -b- sulfonic polyester -b- poly(L-glutamic acid), poly(gamma

methyl-L glutamate) -b- polyurethane -b- poly(gamma
methyl-L glutamate, poly(L-phenylalanine) -b-
polyethylene imine -b- poly(L-phenylalanine), poly(L-
phenylalanine) -b- polymethyloxazoline -b- poly(L-
5 phenylalanine), poly(L-alanine) -b- polycaprolactone -b-
poly(L-alanine), polyglycine -b- polycaprolactone -b-
polyglycine, poly(L-valine) -b- poly(ethylene oxide co
propylene oxide) -b- poly(L-valine), and salts thereof.